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The research on syntheses and properties of novel epoxy/polymercaptan curing optical resins with high refractive indices

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Abstract

A novel thioether glycidyl resin bis[3-(2,3-Epoxypropylthio)phenyl]-sulfone (BEPTPhS) with high refractive index was synthesized by condensation of bis(3-mercaptophenyl)sulfone (BMPS) with epichlorohydrin. It's structure was characterized by FTIR, MS and NMR. It was the first time that trimercaptothioethylamine (TMTEA) was used as curing agent to cure epoxy resins. Optical resins possessing high refractive index were prepared by curing diglycidyl ether of bisphenol A (DGEBA) with the mixture of TMTEA and ethylendiamine (EDA) and by curing BEPTPhS/DGEBA with TMTEA. The research on the optical properties of resins of DGEBA cured by the mixtures of TMTEA and EDA indicated that these resins possess higher refractive index ($n_d > 1.60$), lower dispersity ($\nu_d > 34$), high impact strength (IPS > 30 kJ m^{-2}) and higher transmittance. The n_d, ν_d and density of these resins varied linearly with the EDA content in the curing agent mixtures. The optimum ratio of the EDA content to that of TMTEA is 20:80 (molar ratio), at this ratio the cured resin has the optimum optical properties ($n_d^{20} = 1.61$, $\nu_d = 35.4$). The cured resins of BEPTPhS/TMTEA have a high refractive index (the highest is $n_d = 1.67$). The optical, physical and thermal properties of the cured optical resins of BEPTPhS/TMTEA were discussed in this paper.

Keywords: Epoxy resin/polymercaptan; High refractive index; Optical resins

1. Introduction

Since plastics are lightweight, fragmentation-resistant and easy to be dyed in comparison with glasses, they have been developed rapidly in recent years for the application as optical elements such as lenses of eyeglasses and cameras [1,2]. However, the refractive index of the normally used resins is smaller than 1.50, so it is needed to develop new type of optical resins which possess high refractive index and low dispersion (with less chromatic aberrion). The best way to raise the refractive index of the optical resins is to introduce sulfur element into polymer structure, as the sulfur-containing resins have properties of high refractive index, low dispersion, lightweightness and good heat stability [3–9].

Epoxy resins possess the advantage of chemical resistance, small shrinkage, good heat resistance and excellent mechanical properties. So, in recent years, they are used as optical materials such as optical disk matrix, lenses and prisms [10–12]. However, the refractive index of the conventional epoxy resins is lower, the applications of these resins as optical materials such as lenses where high refractive index is required are limited. So it is needed to synthesize new optical epoxy resins, which possess high refractive index, good mechanical and good heat properties.

In this article a novel epoxy resin possessing high refractive index was synthesized from bis(3-mercaptophenyl)sulfone (BEPTPhS) and epichlorohydrin. The structure of BEPTPhS was characterized by IR, ^{1}H-NMR, ^{13}C-NMR and MS. Trimercaptotriethylamine (TMTEA) was also synthesized from triethanolamine, and used as curing agent to prepare high refractive index optical materials. The reaction of the mercapto group with the epoxy group was similar to that of the hydroxy group. But as the nucleophilicity of sulfur was stronger than that of oxygen, polymercapto compound can cure epoxy at room temperature at present of accelerator [13]. Trithiotriethylamine can cure DGEBA slowly at room temperature without any other accelerator because trimercaptothioethylamine, which contains a tertiary nitrogen atom, is an accelerator itself. The mechanical, optical, physical and heat properties of the cured transparent resins were studied. The relationships between the properties of the cured resins and the content of curing agent were also discussed.

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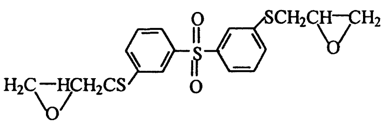
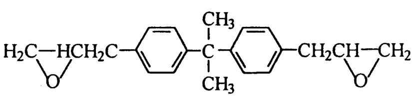
Table 1
The structure and refractive index of curing agents and epoxy resins

The structure of curing agents and epoxy resins	Refractive index
$N(CH_2CH_2SH)_3$ (TMTEA)	1.59
$H_2NCH_2CH_2NH_2$ (EDA)	1.45
 (BEPTPhS)	1.63
 (DGEBA)	1.57

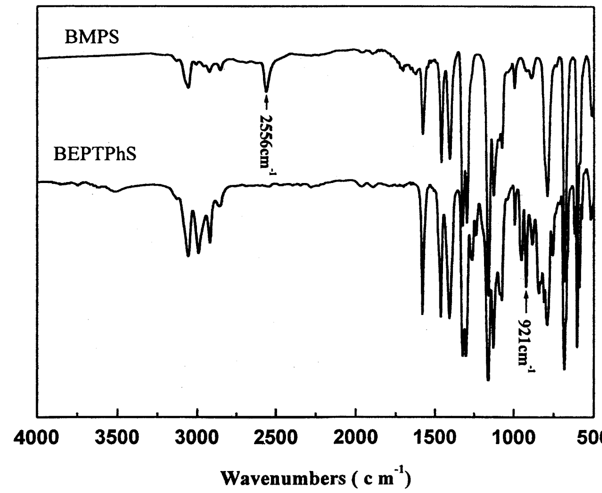


Fig. 1. FTIR spectra of BMPS and BEPTPhS.

2. Experimental

2.1. Materials

Trimercaptotriethylamine (TMTEA) was synthesized as previously reported [14,15], it is a colorless oil liquid, $n_d^{20} = 1.59$. Bis(mercaptophenyl)sulfone (BMPS) was synthesized in our laboratory according to Ref. [16]. Diglycidyl ether of bisphenol A (DGEBA) was purified by fractionation in butanone/methanol solutions, the epoxy equivalent weight (EEW) is 185 g equiv.$^{-1}$. Epichlorohydrin, isopropanol and other reagents were of analytical grade and were used without further purification.

2.2. Synthesis of bis[3-(2,3-epoxypropylthio)phenyl]-sulfone (BEPTPhS)

Twenty-eight grams of BMPS, 78.6 ml of isopropanol and 78 ml epichlorohydrin were placed into a 500 ml four-necked round-bottomed flask. The reaction solution was heated in water bath to 60°C, 2 ml of 20% solution of sodium hydroxide was dropped in within 5 min. After continuously stirring at 60°C for 10 min, another portion of 60 ml of 20% of sodium hydroxide was added for 10 min, and stirred for another 20 min. The organic phase was separated out and 100 ml of toluene added in, then washed with distilled water until neutral. Finally, the solvent and excess epichlorohydrin were distilled out under the reduced pressure. The thiother glycidyl resin (BEPTPhS) is a colorless and transparent viscous liquid, yield 60%, and $n_d^{20} = 1.63$, with the epoxy equivalent weight (EEW) being 200 g equiv.$^{-1}$, which was determined by hydrochlorination method [13]. IR(neat): 921 cm^{-1} (epoxy three-member ring), 1259 cm^{-1} and 1239 cm^{-1} (C–O–C), 1310 cm^{-1} ($-SO_2-$), 2852–3057 cm^{-1} ($-CH_2O$). ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.59 (dd, 2H), 2.80 (t, 2H), 3.14 (d, 2H), 3.15 (d, 2H), 3.18 (m, 2H), 7.43 (t, 2H), 7.60 (d, 2H), 7.75 (d, 2H), 7.96 (t, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 141.89, 138.37, 133.46, 129.70, 127.39, 125.11, 50.68, 46.94, 35.69. MS calcd for $C_{18}H_{18}S_3O_4$ 394.0, found 394.0.

2.3. Preparation of transparent resin samples

Epoxy resins were mixed with curing agent by the same equivalent weight. The mixtures were degassed at 30–40°C, after a short time of cooling, degassed until no bubbles evolved, and then poured into glass mold with rubber gasket (the glass mold was treated with release agent). The glass mold and the mixture sealed inside were heated at 80°C for 4 h, at 100°C for 2 h, at 120°C for 0.5 h and the oven was turn off. After the temperature of the oven fell to room temperature, the mold was removed from the cured resin and a transparent resin plate was obtained.

2.4. Characterization and measurement

2.4.1. Structure characterization of BEPTPhS

The FTIR spectra were recorded on a Nicolet AVATAR360 FTIR Spectrometer, using a KBr plate and measured in atmosphere. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained from a unity-400NMR in $CDCl_3$ solution using tetramethylsilane as an internal reference. The molecular weight was measured on a 4150 mass spectrometer (Finniganmat cop).

2.4.2. Property measurement of transparent cured resins

Refractive index and Abbe's number. The refractive indices (n_d) of the cured resins were measured by a W2S-1 refractometer at 20°C. The Abbe's numbers (ν_d) of the cured resins were calculated using the following formula:

$$\nu_d = (n_d - 1)/(n_F - n_c)$$

where n_d, n_F, n_c are the refractive indices at $\lambda = 589.3$, 486.1, and 656.3 nm, respectively.

UV–Vis transmitance. The ultraviolet visible light spectra

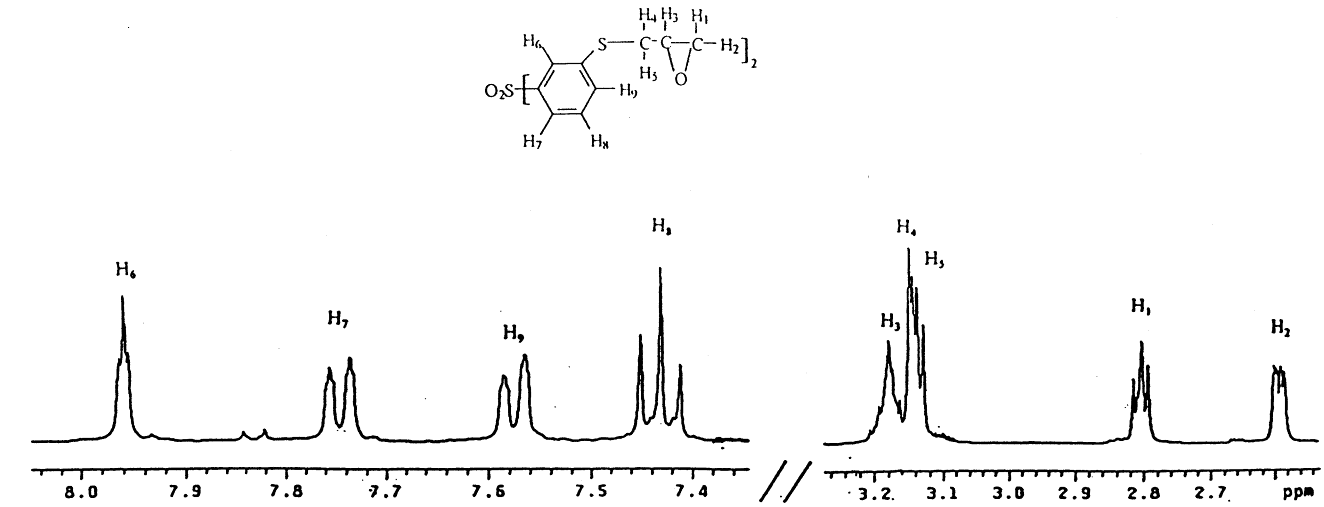


Fig. 2. ^{1}H-NMR spectra of BEPTPhS.

were measured by a Shimadzhu UV3100 Uv–Vis-NIR spectrometer, air as reference; the visible light transmittance of the cured resins was recorded at a wavelength of 550 nm.

Impact resistance. The charpy impact strength of the cured resins were measured by not notched sample on a Xj-40A impact machine made in Changchun, People's Republic of China.

Thermal properties. The glass transmission temperature of the cured resins were obtained from a Perkin–Elmer DSC7 in nitrogen atmosphere at a heating rate of 10°C min^{-1}. TGAs were performed with a Perkin–Elmer TGA7 at a heating rate of 10°C min^{-1} under nitrogen atomosphere from 50 to 750°C.

Surface hardness. Surface hardness was evaluated by pencil hardness.

3. Results and discussion

3.1. Structure characterization of BEPTPhS

The structures and refractive indices of the curing agents and the epoxy resins are shown in Table 1. As shown in Fig. 1, the characteristic band of the epoxide ring was observed at 921 cm^{-1}. At the same time the characteristic absorption peak of the ν_{as}(–C–O–C–) appeared at 1259 cm^{-1}. Furthermore the characteristic band assigned to the –CH_2– stretching of the epoxide ring was observed at 2852–3057 cm^{-1}. The characteristic peak of the hydroxy group dose not appear in the spectrum, this indicated that the reaction was carried out completely. Fig. 2 is the ^{1}H-NMR spectra of BEPTPhS. The chemical shift and the splitting pattern of the ^{1}H-NMR spectrum of BEPTPhS is 2.59 ppm (2H,dd), 2.80 ppm (2H,t), 3.14 ppm (2H,d), 3.15 ppm (2H,d), 3.18 ppm (2H,m), 7.43 ppm (2H,t), 7.60 ppm (2H,d), 7.75 ppm (2H,d), 7.96 ppm (2H,t). The ^{13}C-NMR spectra of BEPTPhS is shown in Fig. 3. No attempt was made to assign each ^{13}C peak of the BEPTPhS molecular, however, the ^{13}C-NMR spectra correspond to the structure of BEPTPhS. The MS calcd for $C_{18}H_{18}S_3O_4$ 394.0, found 394.0.

The characteristic bands in the FTIR spectra, the characteristic peaks in the ^{1}H-NMR and ^{13}C-NMR, and the mass spectrometric analysis correlate sufficiently well with the proposed structure of BEPTPhS in Table 1.

3.2. The properties of the DGEBA/TMTEA/EDA cured resins

The DGEBA/TMTEA/EDA curing system is a new type of self-accelerated curing system of epoxy resins. Ethylenediamine (EDA) was mixed with TMTEA as curing agent to improve the heat resistance and the surface hardness of cured resins.

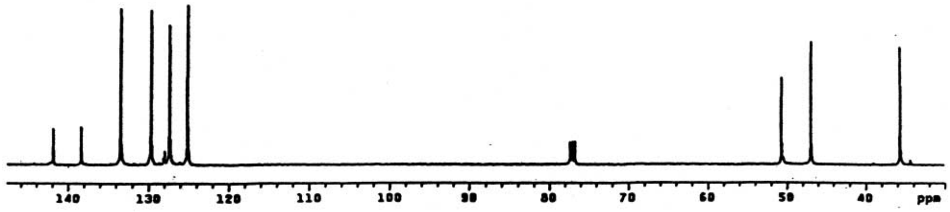


Fig. 3. ^{13}C-NMR spectra of BEPTPhS.

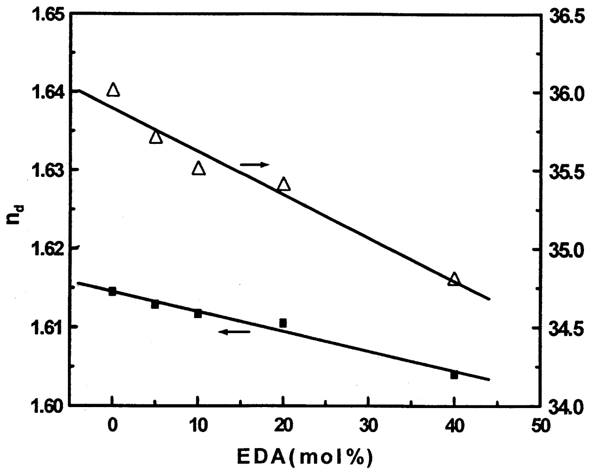


Fig. 4. The variation of refractive index and Abbe number of DGEBA/TMTEA/EDA cured resins with the content of EDA.

The refractive indices of the cured resins of this system are shown in Fig. 4. It can be seen that these series of cured resins have higher refractive indices and low dispersities. The refractive index (n_d) and the Abbe's number (ν_d) are 1.6145 and 36.0, respectively, as the DGEBA was cured by pure TMTEA. With the increase of the content of EDA (the content of EDA is calculated by the molar percentage of the EDA in all curing agent), the refractive index and the Abbe's number decrease linearly (Fig. 4). As the content of EDA increased to 40%, the refractive index and the Abbe's number of the cured resins decreased to 1.604 and 34.8, respectively. The change of the refractive index and the Abbe's number are small. When the content of EDA was greater than 40%, the curing time of the DGEBA/TMTEA/EDA curing system decrease apparently and it was difficult to pour into glass mold. So we only obtained the cured resins with the content of EDA up to 40% in all curing agent.

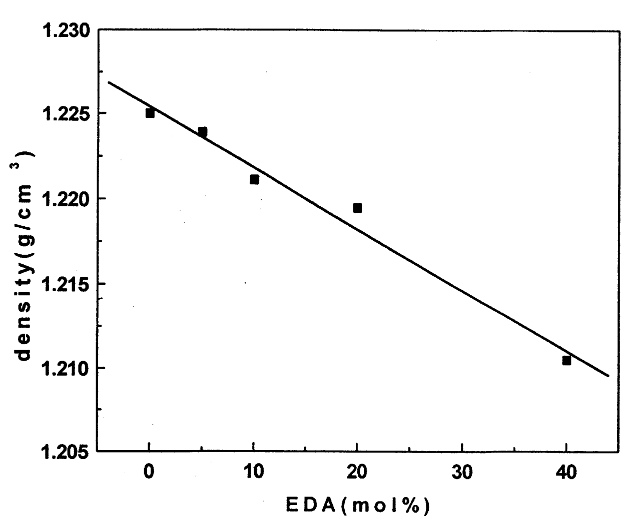


Fig. 5. The variation of density of DGEBA/TMTEA/EDA cured resins with the content of EDA.

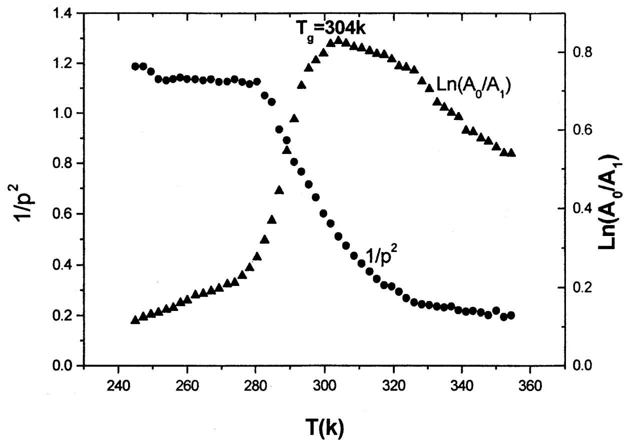


Fig. 6. The TBA graph of DGEBA/TMTEA cured resin.

The densities of these series of the cured resins decrease with the increasing content of EDA (Fig. 5), the density of cured DGEBA resin by pure TMTEA is the highest about 1.225 g cm^{-3}. The TMTEA contains three sulfur atoms, which have a high specific gravity, and so the resins cured by it also possess high densities. From Table 1, it can be seen that the cured resins have high impact strength (IPS), the IPS of the cured DGEBA by pure TMTEA reached 57 kJ m^{-2}. The IPS of the cured resins decrease with the increase of the content of EDA. As the content of EDA increase up to 20%, IPS of the cured resin becomes 31 kJ m^{-2}. This is related to the crosslinking density of the cured resins, as the addtion of EDA increased the crosslinking density of the cured resins. The glass transition temperature (T_g) of the cured resin of DGEBA cured by pure TMTEA is 44.7°C (Fig. 6), which is slightly low. The addition of EDA can increase the T_g of the cured resins. As the content of EDA in the curing agent reached to 20%, the T_g of the cured resin increased to 61.5°C. The addtion of EDA can also raise the heat resistance of the cured resins (Table 2). The heat resistance of the cured resin of DGEBA

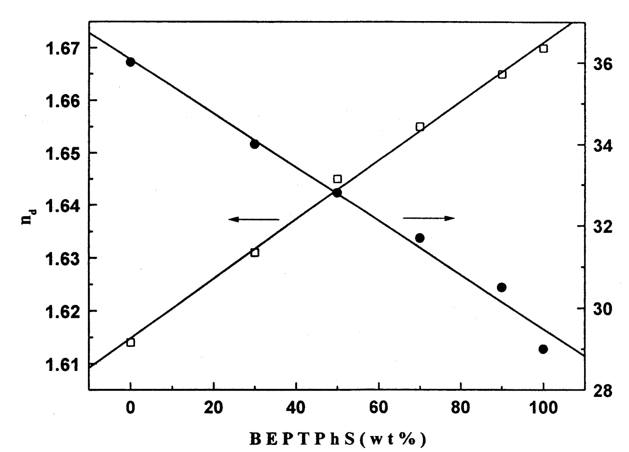


Fig. 7. Variation of refractive index (n_d^{20}) and Abbe's number (ν_d) of BEPTPhS/DGEBA /TMTEA cured resins.

Table 2
Some properties of DGEBA/TMTEA/EDA cured resins

EDA mor%	Rwa[a] (wt%)	T_g[b] (°C)	IPS[c] (kJ m^{-2})	Surface hardness	Trans[d] T%	T_d[e] (°C)	US[f] (nm)
0%	0.2538	44.7	57	HB	90.0	185	314
5%	0.2324	–	–	HB	87.8	–	313
10%	0.1986	50.0	53	HB	88.6	–	303
20%	0.1896	61.5	31	HB	90.0	195	304
40%	0.1421	71.3	–	H	82.4	220	305

[a] Rwa: water absorption of cured resins measured by weight of water absorbed at the percentage of the weight of cured resins.
[b] T_g: the glass transition temperature of cured resins.
[c] IPS: impact strength measured by a XJ-40a impact machine with no notch on the test sheet.
[d] T%: transmittance of cured resins at a wavelength of 550 nm.
[e] T_d: the onset of degradation temperatures.
[f] US: the onset wavelength of total absorption.

cured by TMTEA was obtained by TGA. The onset temperature of weightloss is 185°C. As the content of EDA reach 40%, the onset temperature of weightloss of the cured resin increased to 220°C. The reason may be that the increase of the EDA content increased the cross-linking density of the cured resins. In addition, the transmittances of the cured resins are high up to 90%.

3.3. The properties of BEPTPhS/DGEBA/TMTEA cured resins

As BEPTPhS has a high refractive index, the refractive index of the cured resin of BEPTPhS mixed with DGEBA and cured by TMTEA is also higher. It reached to 1.67 when pure BEPTPhS was cured by TMTEA. Hence BEPTPhS can be mixed with DGEBA to increase the refractive index. As shown in Fig. 7, the refractive index of the cured resins increased linearly with the increase of the content of BEPTPhS, The Abbe's number decreased with the increase of the content of BEPTPhS (the content of BEPTPhS is calculated by the weight percentage of BEPTPhS in total weight of all epoxy resins). The other properties of the BEPTPhS/DGEBA/TMTEA cured resins are shown in Table 3. It can be seen that the densities of this series of the cured resins increase linearly with the increasing content of BEPTPhS and the onset total-absorption wavelengths of these resins shift toward the longer wavelengths, as the content of BEPTPhS increase with the highest onset wavelength reached to 359 nm. The water absorption of the cured resins of the mixture of BEPTPhS and DGEBA is greater than that of pure DGEBA, as the BEPTPhS contain the hydrophilic sulfone groups. The surface hardness of the cured resin by the pure BEPTPhS is lower, the addition of DGEBA can increase the surface hardness of the cured resins (Table 3). The results of DSC and TBA measurement showed that T_g of the cured resin of the pure BEPTPhS cured by TMTEA was slightly lower. The T_g of the cured resin were 37.2°C measured by DSC and 41.4°C by TBA, respectively. From the T_g of the cured resin it can be seen that these series of resins can be used as optical material where low glass transition was needed.

4. Conclusion

The polymercaptan TMTEA, which is a tertiary amine, has a higher refractive index ($n_d = 1.59$) and self-catalytic effect. It can be used as epoxy curing agent to cure epoxy resin rapidly without addition of any other accelerator. The high refractive index of the cured DGEBA by pure TMTEA reached to 1.61, at the same time the cured resin has a low dispersity. TMTEA can be mixed with EDA to increase the surface hardness and the heat resistance of the cured DGEBA resins. The novel epoxy resin BEPTPhS has a higher refractive index ($n_d = 1.63$). The refractive index of the pure BEPTPhS cured by TMTEA reached to 1.67.

Table 3
Some properties of BEPTPhS/DGEBA/TMTEA cured resins

DGEBA (wt%)	Density (g cm^{-3})	Rwa[a] (wt%)	Surface hardness	Trans[b] T%	US[c]
0	1.3799	0.457	HB	76.7	359
10	1.3598	0.748	H	80.0	358
30	1.3183	0.563	H	81.6	357
50	1.2962	0.573	2H	82.4	355
70	1.2771	0.628	2H	84.5	354
100	1.2250	0.254	HB	90.4	314

[a] Rwa: water absorption of cured resins measured by weight of water absorbed at the percentage of the weight of cured resins.
[b] T%: transmittance of cured resins at a wavelength of 550 nm.
[c] US: the onset wavelength of total absorption.

The surface hardness of the cured BEPTPhS resins can be improved by the addition of DGEBA. The curing reaction kinetics of BEPTPhS/TMTEA curing system will be published in the following paper.

Acknowledgements

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